Conversion of Soybean Oil into Ion Exchange Resins: Removal of Copper (II), Nickel (II), and Cobalt (II) Ions from Dilute Aqueous Solution Using Carboxylate-Containing Resin

Z. S. LIU, S. Z. ERHAN

Oil Chemical Research, NCAUR, ARS, USDA, 1815 North University Street, Peoria, Illinois 61614

ABSTRACT: An ion-exchange resin containing carboxylic acid groups was prepared by reaction of epoxidized soybean oil with triethylene tetramine, followed by hydrolysis of glycerides by using sodium hydroxide solution. The cation exchange capacity of the resins was determined to be 3.50 mequiv/g. The adsorption capacity for Cu^{2+}, Ni^{2+}, and Co^{2+} on the obtained resin at pH 5.0 was found to be 192, 96, and 78 mg/g, respectively. Effect of pH on the adsorption capacity for copper (II), nickel (II), and cobalt (II) ions were also studied. Cu^{2+}, Ni^{2+}, and Co^{2+} were adsorbed at a pH above 3. These metal ions adsorbed on the resin are easily eluted by using 1N HCl solution. The selectivity of the resin for Cu^{2+} from mixtures containing $Cu^{2+}/Co^{2+}/Ni^{2+}$ ions in the presence of sodium chloride was also investigated. © 2002 Wiley Periodicals, Inc. J Appl Polym Sci 84: 2386–2396, 2002

Key words: epoxidized soybean oil; triethylene tetramine; ion-exchange; selectivity; sodium chloride

INTRODUCTION

The importance of natural products for industrial applications becomes very clear with increasing social emphasis on the issues of environment, waste disposal, and the depletion of nonrenewable resources. The United States agriculture produces over 12 billion pounds of soybean oil annually, and frequently carry-over exceeds one billion pounds. Currently, only 300 million pounds of soybean oil are used in industrial ap-

plications. The development of new economically feasible industrial products from vegetable oils or commercial processes is the objective of continued research in both the public and the private sector. Vegetable oils are currently used in various industrial applications such as printing inks,[1,2] biodiesel,[3,4] and lubricants.[5] Preparation of vegetable oil based polymers for ion exchange resin applications has rarely been reported. The carboxylic acid functionality groups are, indeed, the usual origin of cation-exchange capacity in natural products. For example, alginic acid (which is extracted on a large scale from seaweeds for use as a thickening and emulsifying agent) is a giant carbohydrate built from mannuronic acid units. Liu and Rempel[6,7] reported preparation of crosslinked acrylic acid and acrylamide copolymer and its application to remove copper (II), cobalt (II), and nickel (II) ions from dilute aqueous solutions. Maxim and coworkers[8] reported

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the retention process of the copper (II) and nickel (II) cations from $CuSO_4$ and $NiSO_4$ aqueous solution by eight acrylic ion exchangers. They also studied the elution process of these cations with $0.5M$ HCl solution. Horák and coworkers[9] recently reported the synthesis of a highly Cu^{2+}-selective ion exchange resin based on poly(glycidyl methacrylate-*co*-ethylene dimethacrylate)-containing derivatives of aspartic acid as the chelating ligand. This ion exchanger combines a high selectivity for Cu^{2+} over Zn^{2+} and Cd^{2+} ions with fast exchange kinetics.

Here, we report the preparation of a novel ion exchange resin produced by reacting epoxidized soybean oil (ESO) with triethylene tetramine (TETA), followed by hydrolysis of glycerides with $0.4N$ sodium hydroxide solution. Consequently, this new ion exchange resin's ability to absorb transition metals such as copper (II), nickel (II), and cobalt (II) and its relative absorption of mixture of three metal ions in the presence of salt (NaCl) in the solution were examined. In hydrometallurgy, the separation of copper from cobalt and nickel is of considerable importance. The need for more highly specific metal recovery processes in both hydrometallurgical and environmental applications has led to an increasing interest in selective ion exchange. Finally, kinetic data on the sorption and elution of sorbed copper (II), nickel (II), and cobalt (II) ions are reported.

EXPERIMENTAL

Reagents

ESO was obtained from Elf Atochem Inc. (Philadelphia, PA) and used as received. Cupric sulfate ($CuSO_4$ 5 H_2O), nickel sulfate ($NiSO_4$ 6 H_2O), cobalt sulfate ($CoSO_4$ xH_2O), and TETA (60% tech) were obtained from Aldrich Chemical Co. (Milwaukee, WI) and used as received.

Sorbent

The resin used in this work was prepared by reaction of ESO with TETA, followed by hydrolysis of glycerides using $0.4N$ NaOH solution. As depicted in Scheme 1, a mixture of ESO (140.6 g, 0.141 mol) and TETA (40.3 g, 0.165 mol) was stirred at room temperature for 1 h. Then, the solution was poured into a $21.6 \times 15.24 \times 3.18$ cm mold. The mixture in the mold was cured overnight at 100°C and then at 140°C for 48 h. The resulting solid was ground into powder ($<$ 20 mesh), referred to as ESOT-I resin. Hydrolysis of ESOT-I resin was accomplished by refluxing a stirred mixture of ESOT-I resin (12 g) in $0.4N$ NaOH solution (360 mL) at 100°C for 20 h. After cooling the solution to room temperature, the product was precipitated by neutralizing the solution with $1N$ HCl. The resulting solid was washed with deionized water and ethanol and dried to a constant weight at 100°C to give 9.5 g of a light yellow solid. The solid was ground into $<$ 60 mesh powder, referred to ESOT-II resin. The density of ESOT-II resin was determined to be 1.3978 g/cm^3. The cation exchange capacity of ESOT-II resin, determined according to the method described by Kunin,[10] was 3.50 mequiv/g.

Instrumentation

Concentrations of copper (II), cobalt (II), and nickel (II) ions in solution were determined by using a Perkin–Elmer emission spectrometer plasma 400 ICP. IR spectra were recorded with a Perkin–Elmer Spectrum RX FTIR spectrometer.

Infrared Spectra Analysis

Infrared spectra (IR) of ESOT-I and ESOT-II were recorded as KBr pellets and the spectrum of ESO was run as neat liquid. Infrared spectrum of ESO shown in Figure 1(a) can be compared to the spectrum of ESOT-I, shown in Figure 1(b). As can be seen, the characteristic oxirane absorption at 823.3 cm^{-1} in ESO is not present in ESOT-I due to the ring-opening reaction with TETA's amine groups. The IR spectrum of ESOT-II in Figure 1(c) obtained after hydrolysis of ESOT-I resin showed a shift in the ester carbonyl band to 1718.9 cm^{-1} from 1734.5 cm^{-1} when compared to ESOT-I, due to strong H-bonding of the carboxylic acids as dimers. Hydrogen bonding and resonance weaken the C=O bond, resulting in absorption at a lower frequency.

Sorption Experiments

In all equilibrium studies, measured amounts of sorbent were vigorously shaken with definite solution volumes of known metal concentrations for 20 h in tightly stoppered glass bottles at 25°C, using a platform shaker operating at 300 rpm. The residual metal concentrations in solution were then measured. For each of the metal species, Cu(II), Ni(II), and Co(II), a range of concentrations (1–8 mM) was employed for the study. The pH values of the $CuSO_4$, $NiSO_4$, and $CoSO_4$
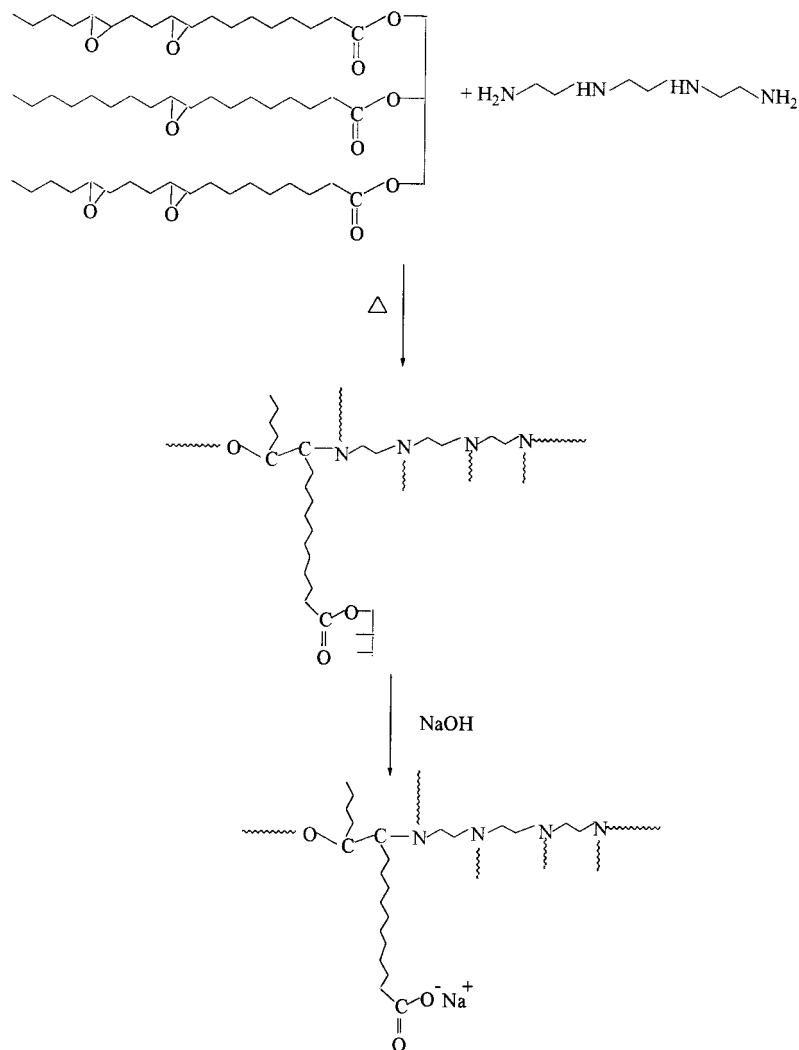
Scheme 1

solutions ranged from 5.0 to 5.45. The sorption was also measured as a function of time under vigorous agitation.
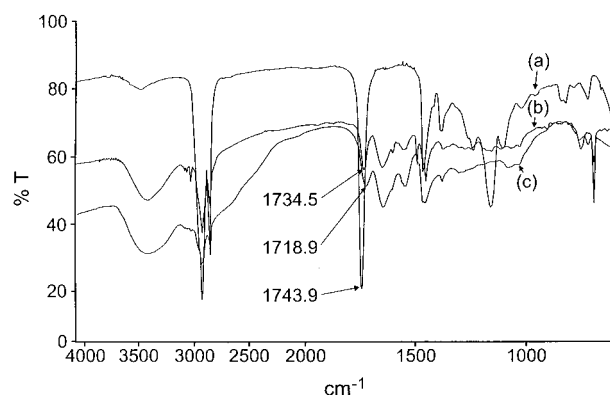

Figure 1   Infrared (IR) spectra of ESO, ESOT-I, and ESOT-II

The sorption capacity of ESOT-II resin for copper (II), nickel (II), and cobalt (II) was determined by agitating the resin (0.50 g) in excess 0.1M CuSO$_4$, 0.1M NISO$_4$, and 0.1M CoSO$_4$ solution (50 mL), respectively, for 20 h and measuring the copper, nickel, and cobalt contents of the respective sorption products. The results show that the sorption capacities of ESOT-II resin for copper (II), nickel (II), and cobalt (II) are 192, 96, and 78 mg/g, respectively.

Sorption Selectivity Experiments

In the sorption selectivity experiments, measured amounts of the sorbent were vigorously shaken with definite solution volumes containing known metal concentrations (combinations of three metals at a time), in 1M of sodium chloride, for 20 h in tightly stoppered glass bottles at 25°C, using a platform shaker operating at 300 rpm. The resid-
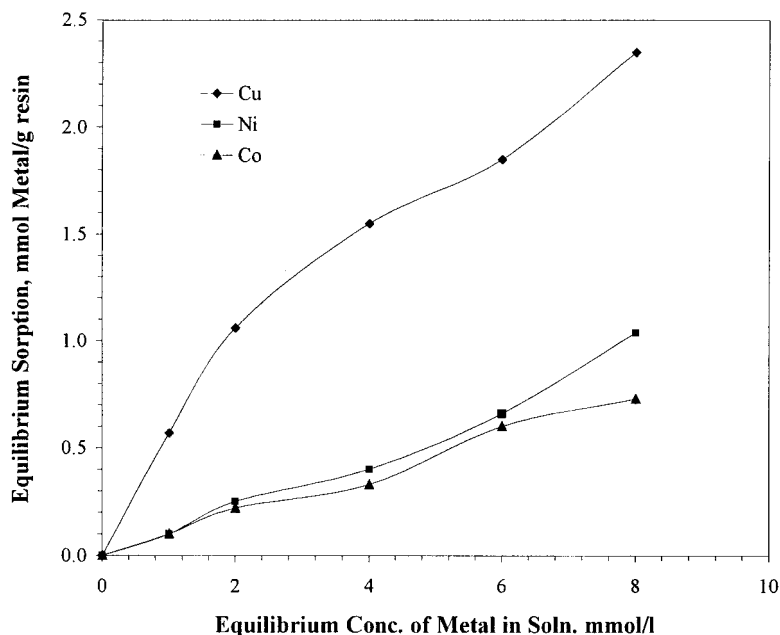
Figure 2 Equilibrium sorption of copper, cobalt, and nickel from sulfate solutions on ESOT-II resin. Resin loading, 1.5 g L^{-1}; temperature, 25°C.

ual metal concentrations in solution were then measured. A range of metal concentrations (1–10 mM) was employed for this experiment.

pH Runs

Sulfuric acid was used to acidify the solution; the pH range employed for the pH profiles ranged from 1.66 to 6.16. Once 20 mL of the metal solution (6 mM metal) was added, the bottles were placed evenly on a platform shaker operating at 300 rpm for 20 h at 25°C. The residual metal concentrations in solution were then measured.

Stripping of Metals

In the stripping experiments, 0.04 g ESOT-II, on which 192 mg Cu^{2+}/g, 96 mg Ni^{2+}/g, or 78 mg Co^{2+}/g was sorbed, were shaken (300 rpm) in the presence of 1N HCl (20 mL) solution on a platform shaker at 25°C. The time was started when the acid solution first hit the resin particles; the bottles were removed at 15-min, 30-min, 1-h, 2-h, 3-h, and 4-h intervals and metal concentrations in the solutions were measured.

RESULTS AND DISCUSSION

Sorption Isotherm

The sorption isotherm was studied at 25°C by using metal concentrations between 1 mmol/L

and 8 mM at pH 5.01–5.45. The equilibrium data for copper (II), nickel (II), and cobalt (II) sorption from aqueous solutions by ESOT-II resin are plotted against equilibrium solution in Figure 2. The results show the acidic cation-exchange resin ESOT-II can take up significant quantities of copper (II), but relatively lower amounts of nickel (II) and cobalt (II). The sorption capacity of ESOT-II resin for Cu^{2+}, Ni^{2+}, and Co^{2+} are in the order Cu^{2+} > Ni^{2+} > Co^{2+}, respectively.

The sorption data with respect to copper (II), nickel (II), and cobalt (II) are fitted well by a Freundlich isotherm, whereas copper (II) is also fitted well by Langmuir isotherm. However, sorption data with respect to nickel (II) and cobalt (II) are fitted poorly by a Langmuir isotherm. Thus, for the sorption of copper (II), nickel (II), and cobalt (II), the Freundlich isotherm may be written as:

$$X^* = mC^{*n} \tag{1}$$

where X^* and C^* are the equilibrium sorption and equilibrium concentration of sorbate, respectively, and m (mmol/g dry resin) and n are adjustable parameters. To solve the isotherm constants, the function may be linearized by taking the natural logarithm of each side in eq. 1 to obtain:

$$\ln X^* = \ln m + n \ln C^* \tag{2}$$

Table I   Parameters of Freundlich and Langmuir Isotherm for Sorption on ESOT-II ($T = 25°C$)

Sorbate	Freunlich Isotherm			Langmuir Isotherm		
	m (mmol/g resin)	n	R^2	As (mmol/g resin)	K_b (l mmol^{-1})	R^2
CuSO$_4$	0.6109	0.6501	0.9845	3.862	0.1742	0.964
NiSO$_4$	0.1042	1.063	0.9851	—	—	—
CoSO$_4$	0.1032	0.9417	0.9853	—	—	—

Values of m and n were determined by linear regression. The results are given in Table I. For the sorption of copper (II), the Langmuir isotherm may be written as:

$$C_A^*/X^* = 1/K_b A_s + C_A^*/A_s \qquad (3)$$

where X^* and C_A^* are, respectively, the equilibrium sorption (mmol/g resin) and equilibrium concentration (mmol/L) of metal ion in solution. The values of the saturation constant, A_s (mmol/g resin), and the binding constant, K_b (1 mmol^{-1}), were determined by linear regression. They are also presented in Table I.

Effect of Salt on Sorption Capacity

Useful information regarding the salt effects can be obtained by measuring sorption capacity in the presence of sodium chloride. The effects of adding NaCl at concentrations of 0.5 and 1.0M on the sorption capacity of ESOT-II for copper (II) and NaCl at concentrations of 1.0M for nickel (II) and cobalt (II) were examined. Figures 3, 4, and 5 graphically show how the sorption isotherm changes by the addition of NaCl. In the case of copper (II), NaCl hardly affects the copper (II) sorption on ESOT-II resin over the whole range of sorbate concentrations employed. However, nickel (II) and cobalt (II) sorption on ESOT-II resin decrease upon addition of 1M NaCl over the whole range of sorbate concentrations employed. The results of this study clearly show that, in the presence of NaCl, the separation of copper (II) from nickel (II) and cobalt (II) ions by using ESOT-II resin is possible.
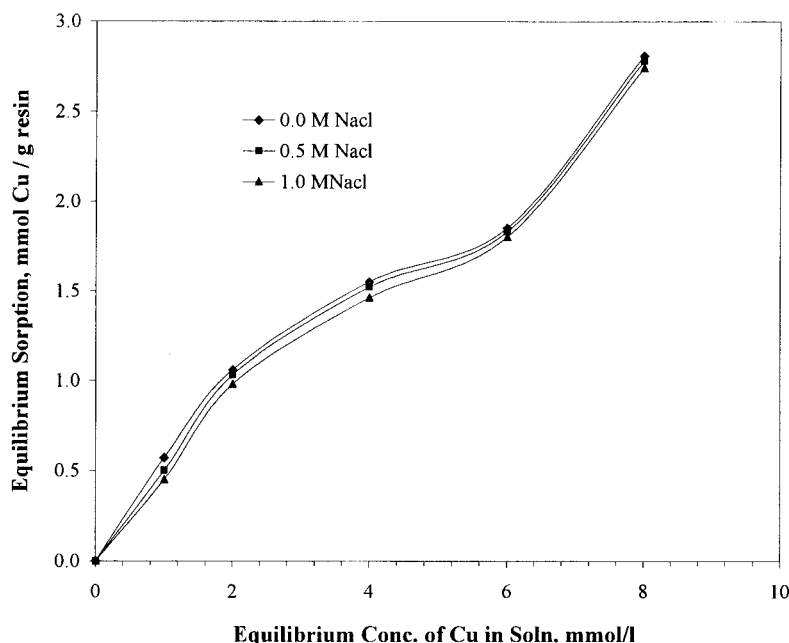

Figure 3   Equilibrium sorption of copper from CuSO$_4$, CuSO$_4$ in 0.5M NaCl and 1.0M NaCl solutions on ESOT-II resin. Resin loading, 1.5 g L^{-1}; temperature, 25°C.
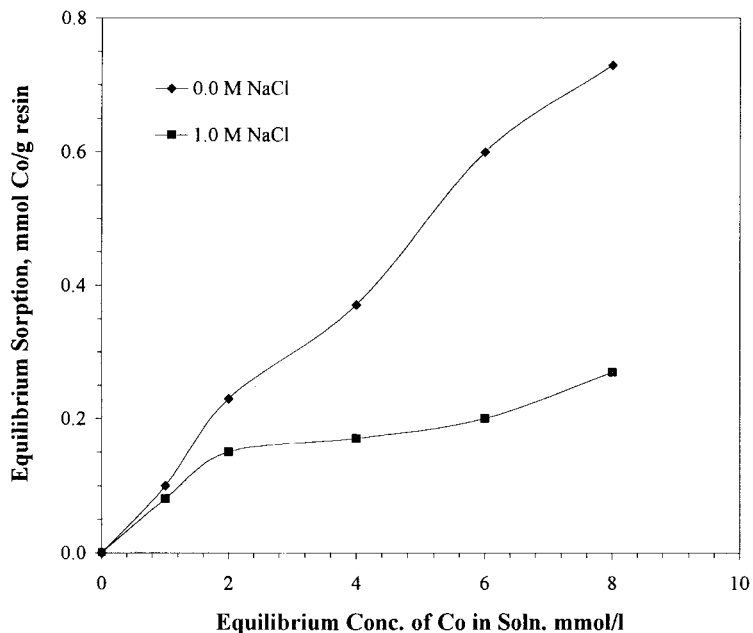
Figure 4 Equilibrium sorption of nickel from $NiSO_4$, in 0.0*M* NaCl and 1.0*M* NaCl solutions on ESOT-II resin. Resin loading, 1.5 g L^{-1}; temperature, 25°C.

Selectivity of ESOT-II

Because considerable interest exists in the separation of copper from nickel and cobalt, the selectivity of ESOT-II resin toward solution containing the mixed copper (II), nickel (II), and cobalt (II) ions in the presence of salt (1.0*M* NaCl) were

investigated. Figure 6 shows that ESOT-II resin absorbs about eight times more copper (II) ion than cobalt (II) and nickel (II) ions at higher concentrations (> 4 mM). However, the sorption capacity differences between copper (II), nickel (II), and cobalt (II) ions are also rather large at lower
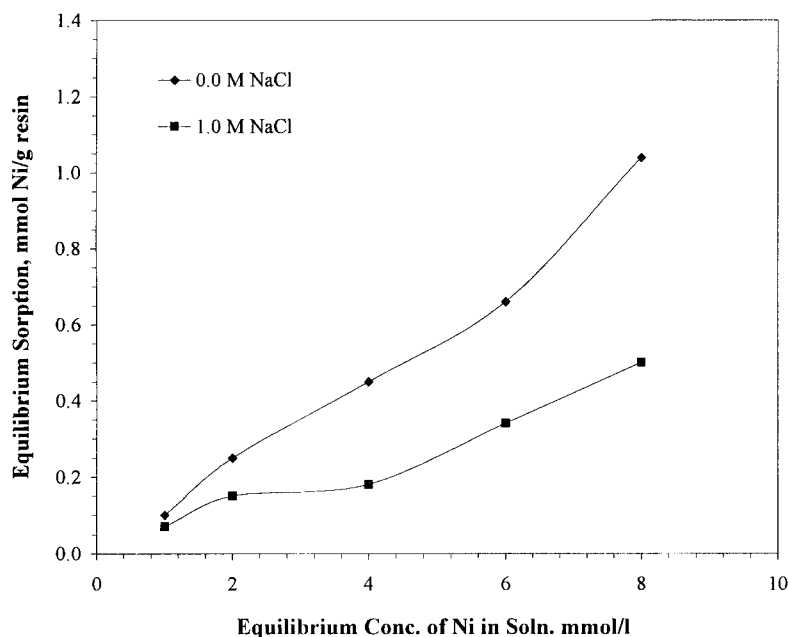

Figure 5 Equilibrium sorption of cobalt from $CoSO_4$, in 0.0*M* NaCl and 1.0*M* NaCl solutions on ESOT-II resin. Resin loading, 1.5 g L^{-1}; temperature, 25°C.
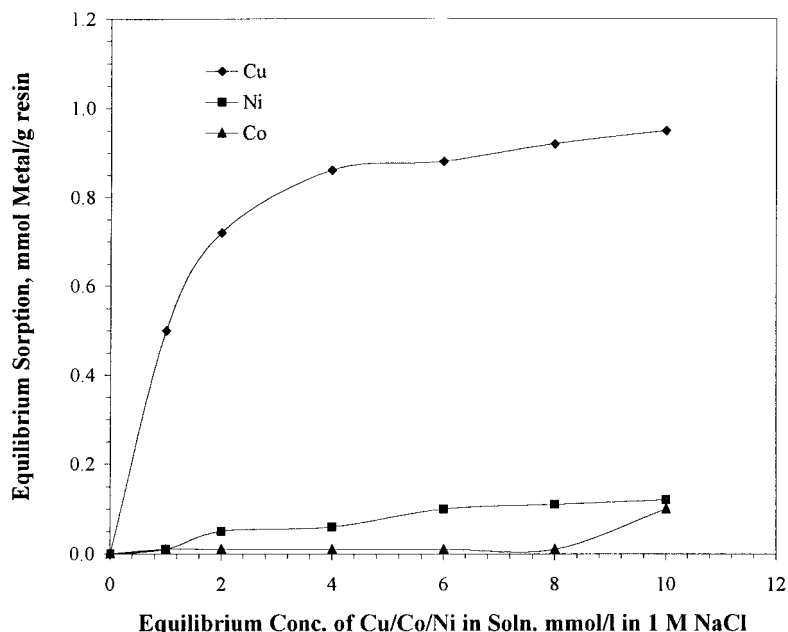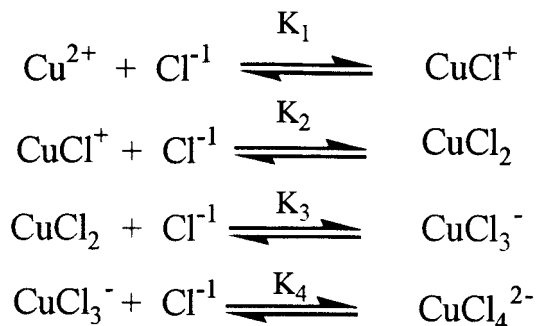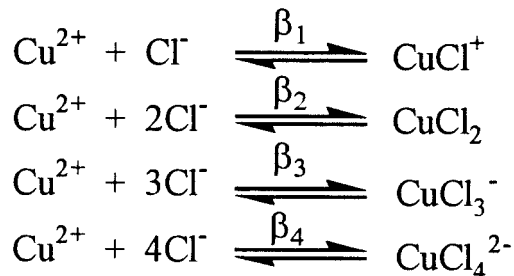
Figure 6   Equilibrium sorption of copper/nickel/cobalt ions from mixed sulfate solution in $1.0M$ NaCl solution using ESOT-II resin. Resin loading, 1.5 g L^{-1}; temperature 25°C.

metal concentrations ($<$ 4 mM), by about five times. One can predict that the separation of copper (II) from nickel (II) and cobalt (II) ions is possible by using ESOT-II resin in the presence of sodium chloride. Liu and Rempel[7] also reported the same trend for selectivity study by using crosslinked acrylic acid and acrylamide copolymers. It is well known that in the presence of Cl^{-1} in solution, the four coordinate M (II) complex is formed. By taking copper as an example, Scheme 2 shows the formation of the four complex species, where K_1 to K_4 are the stepwise formation constants associated with each of these equilibria. The overall formation may be shown as Scheme 3, where β_1 to β_4 are the formation constants associated with equilibria corresponding to the overall

$$Cu^{2+} + Cl^{-} \underset{}{\overset{\beta_1}{\rightleftharpoons}} CuCl^{+}$$
$$Cu^{2+} + 2Cl^{-} \underset{}{\overset{\beta_2}{\rightleftharpoons}} CuCl_2$$
$$Cu^{2+} + 3Cl^{-} \underset{}{\overset{\beta_3}{\rightleftharpoons}} CuCl_3^{-}$$
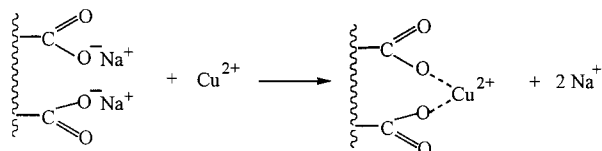$$Cu^{2+} + 4Cl^{-} \underset{}{\overset{\beta_4}{\rightleftharpoons}} CuCl_4^{2-}$$

Scheme 3

reactions. The relations among the β and K values are therefore determined as:

$$\beta_1 = K_1, \quad \beta_2 = K_1K_2, \quad \beta_3 = K_1K_2K_3,$$
$$\beta_4 = K_1K_2K_3K_4$$

If $[C]$ is the total concentration of copper, then

$$[C] = [Cu^{2+}] + [CuCl^{+}] + [CuCl_2] + [CuCl_3^{-}]$$
$$+ [CuCl_4^{2-}]$$

The fraction of Cu(α), presented as each species, may be calculated as a function of $[Cl^{1}]$ alone and is shown as follows:

$$Cu^{2+} + Cl^{-1} \underset{}{\overset{K_1}{\rightleftharpoons}} CuCl^{+}$$
$$CuCl^{+} + Cl^{-1} \underset{}{\overset{K_2}{\rightleftharpoons}} CuCl_2$$
$$CuCl_2 + Cl^{-1} \underset{}{\overset{K_3}{\rightleftharpoons}} CuCl_3^{-}$$
$$CuCl_3^{-} + Cl^{-1} \underset{}{\overset{K_4}{\rightleftharpoons}} CuCl_4^{2-}$$

Scheme 2

Scheme 4

Scheme 6

$$\alpha_0 = [Cu^{2+}]/[C] = (1 + \beta_1[Cl^-] + \beta_2[Cl^-]^2$$

$$+ \beta_3[Cl^-]^3 + \beta_4[Cl^-]^4)^{-1}$$

$$\alpha_1 = [CuCl^+]/[C] = \beta_1[Cl^-]\alpha_0$$

$$\alpha_2 = [CuCl_2]/[C] = \beta_1[Cl^-]^2\alpha_0$$

$$\alpha_3 = [CuCl_3^{-1}]/[C] = \beta_1[Cl^-]^3\alpha_0$$

$$\alpha_4 = [CuCl_4^{2-}]/[C] = \beta_1[Cl^-]^4\alpha_0$$

Because ESOT-II is a weak acid cation exchange resin, it could not exchange with $[CuCl_2]$, $[CuCl_3^-]$, and $[CuCl_4^{2-}]$ anionic complex species. The four stepwise formation constants may be obtained from literature.[11] Liu and Rempel[7] calculated the relative fractions of each copper, nickel, and cobalt complex species and found the relative fraction value for $CuCl^+$ is much larger than for Cu^{2+} and also is much larger than for either $CoCl^+$ or $NiCl^+$ at 0.5 and $1M$ NaCl solution. When ESOT-II resin reaction with strong base, such as NaOH, converts some of the carboxylic groups into a more highly ionized COO^-Na^+ form. Scheme 4 shows the proposed exchanging process of ESOT-II for exchange with Cu^{2+}. In contrast, NaCl, a neutral salt, only ionizes ESOT-II resin to a very minor degree. This is because one of the products is a highly ionized acid. The solution pH will therefore be low, and as a result, the ionization of the resin will be depressed and driven to the left, as shown in Scheme 5.

Consequently, it only exchanges with $CuCl^+$. Scheme 6 depicts the proposed exchange process. This is the possible explanation of separation of copper from cobalt and nickel.

Effect of pH on Sorption Capacity

The effect of pH on the equilibrium sorption of copper (II), nickel (II), and cobalt (II) by ESOT-II resin is shown in Figure 7. The sorption of copper (II), nickel (II), and cobalt (II) ions on ESOT-II
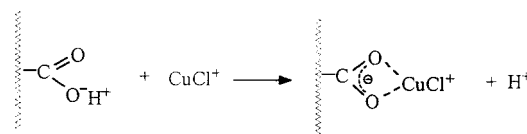
Scheme 5

resin is relatively unaffected by acidic pH down to 3. However, the sorption of copper (II), nickel (II), and cobalt (II) ions on ESOT-II resin is seen to fall drastically at pH levels below 3, which indicates that the sorbed copper (II), cobalt (II), and nickel (II) ions could be easily stripped by dilute acid. These results are in agreement with the observation that weakly acidic ion-exchange resins absorb hydrogen ion more strongly than corresponding metal ions. Therefore, the addition of H^+ ions in a slight excess to the solution may displace all other cations from the resin.

Sorption Rate Behavior

Copper (II), nickel (II), and cobalt (II) sorption on the ESOT-II resin was measured as a function of time under vigorous agitation at ambient temperature. Figures 8, 9, and 10 depict the results. The sorption rate on ESOT-II resin is relatively high for $CuSO_4$; 15% of the equilibrium sorption is attained within 15 min by using 8 mM solution. The sorption rate on ESOT-II resin is relatively lower for $NiSO_4$ and $CoSO_4$, where about 2% the equilibrium sorption is attained within 15 min by using 8 mM $NiSO_4$ or $CoSO_4$ solution, respectively. The copper sorption equilibrium rate appears to be dependent on the solution concentrations.

Stripping Behavior

Stripping agent, a normal hydrochloric acid, was used to remove the metal ions from the resin. By mixing the resin-containing metal ions with the stripping agent at room temperature and subsequently analyzing the solutions for copper (II), nickel (II), and cobalt (II) ions, the efficiency of the stripping agent could be seen. Figure 11 shows that the stripping rate of sorbed copper (II), cobalt (II), and nickel (II) ions is very high. Within 4 h, 95% of the nickel (II) ion and 76% of the cobalt (II) ion can be stripped from ESOT-II resin, whereas 67% of copper (II) ion was stripped. This is in accord with the relatively higher absorption strength of copper ion than cobalt and nickel ions.

CONCLUSION

The carboxylate-containing ESTO-II resin can be used for efficiently removing copper (II), nickel
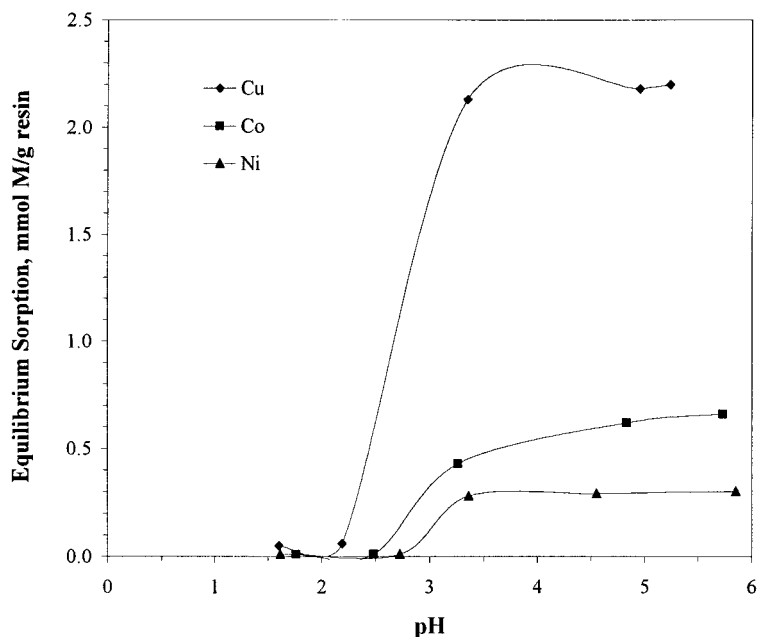
Figure 7 Effect of pH on equilibrium sorption of copper, nickel, and cobalt from sulfate solution on ESOT-II resin. Initial concentration of metals, 6.0 mM. Other conditions as given in Figure 2.

(II), and cobalt (II) ions from dilute aqueous solutions. This resin has a cation exchange capacity of 3.50 mequiv/g, a copper (II) sorption capacity of 192 mg/g, a nickel (II) sorption capacity of 96 mequiv/g, and a cobalt (II) sorption capacity of 78 mg/g. It was found that pH affects the sorption equilibrium of the metals on the resin, and below pH 3, copper (II), cobalt (II), and nickel (II) sorption on the resin falls drastically. This indicates the sorbed metals could be stripped by dilute acid,
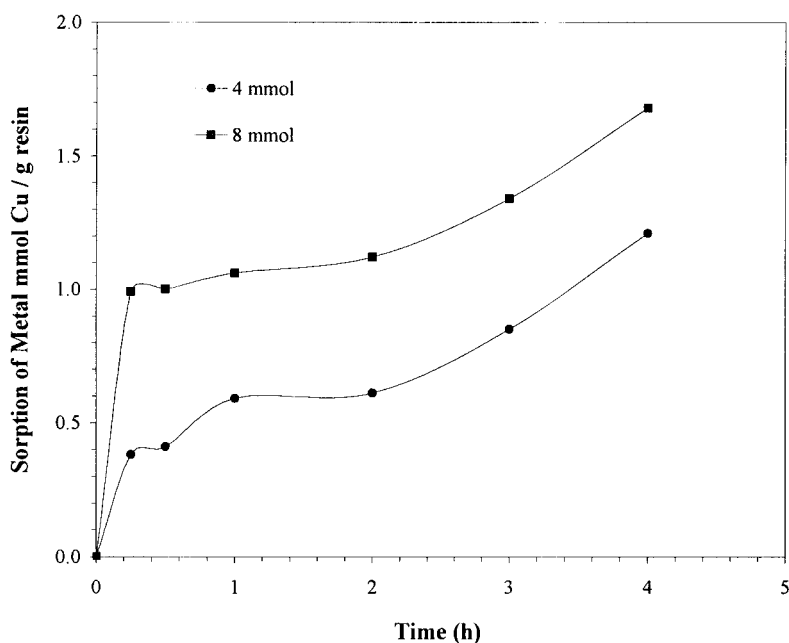

Figure 8 Rate of sorption of copper from sulfate solution by ESOT-II resin. Initial concentration of copper (●) 4.0 mM; (■) 8.0 mM. Other conditions as given in Figure 2.
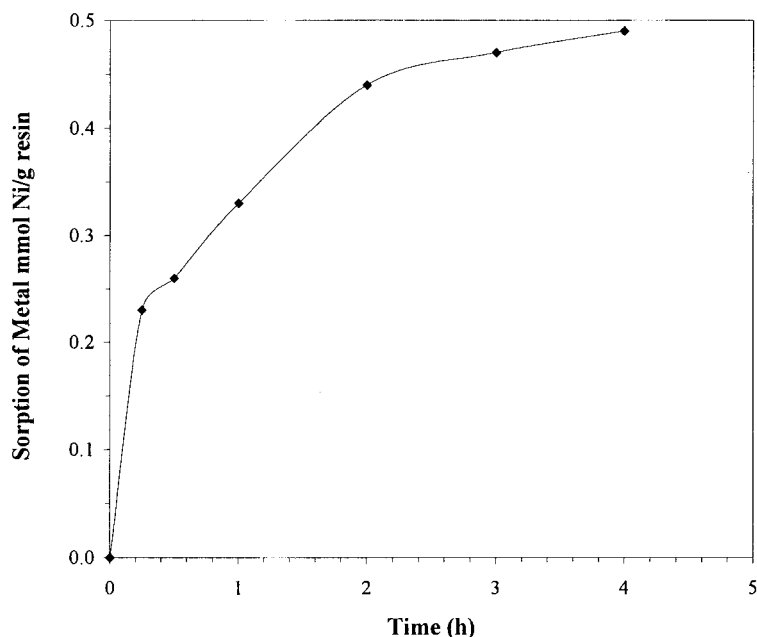
Figure 9 Rate of sorption of nickel from sulfate solution by ESOT-II resin. Initial concentration of nickel, 8.0 mM. Other conditions as given in Figure 2.

and it was found that the nickel (II), cobalt (II), and copper (II) ions sorbed on the ESOT-II resin could be stripped to 95, 76, and 67% with $1N$ HCl in 4 h, respectively. This is in accord with the relatively higher absorption strength of copper (II) ion than nickel (II) and cobalt (II) ions. The results of the salt effect study suggest it is possible to separate copper (II) ion from aqueous $Cu^{2+}/Ni^{2+}/Co^{2+}$ mixture in the presence of NaCl. ESOT-II resin was found to sorb eight times more copper (II) ion than nickel (II) and cobalt (II) ions at higher metal concentrations (> 4 mM). How-
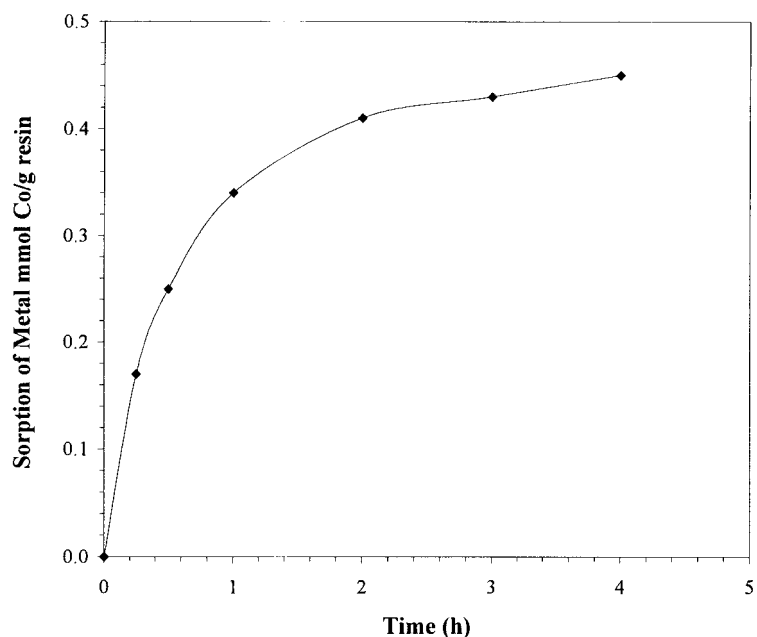

Figure 10 Rate of sorption of cobalt from sulfate solution by ESOT-II resin. Initial concentration of cobalt, 8.0 mM. Other conditions as given in Figure 2.
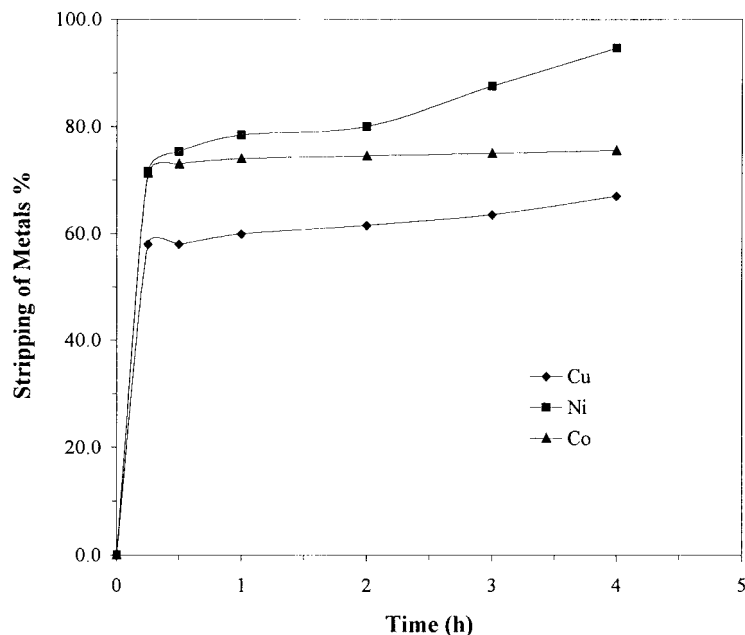
Figure 11   Rates of stripping of ESOT-II resin containing 192 mg/g Cu, 96 mg/g Ni, and 78 mg/g of Co, respectively, under vigorous agitation, in 1N HCl. Resin loading, 2 g L^{-1}; temperature, 25°C.

ever, the sorption capacity difference between copper (II), cobalt (II), and nickel (II) ions are also rather large (five times) at lower metal concentrations (< 4 mM).

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